Theory of Semiclassical Transition Probabilities (S Matrix) for Inelastic and Reactive Collisions. III. Uniformization Using Exact Trajectories*

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A canonical transformation of coordinates in Part I is made using exact trajectories. The transformation tends to uniformize all coordinates including that for the radial motion, thus removing the singularities in the simple semiclassical exponential wavefunction in typical cases. The new coordinates are "time" and certain constants of the motion. A symmetrical choice for the transformation then yields an integral expression for the S matrix satisfying the principle of microscopic reversibility. Topics discussed include semiclassical unitary transformations and time-reversal properties of action-angle variables and of semiclassical wavefunctions. Applications and numerical tests of the integral expression for S_{mn} are in progress.

I. INTRODUCTION

In Part I we described a method for obtaining a semiclassical expression for the S matrix for inelastic and reactive collisions, using data on exact classical collision trajectories and a semiclassical wavefunction.[1] In a different approach Miller[2] has used instead a semiclassical form of a Feynman propagator.[3] Both treatments have been shown to give similar results for the asymptotic approximation for S-matrix elements S_{mn}.[4]

In the present paper we turn our attention to finding for S_{mn} an integral expression which, like its asymptotic approximation, satisfies the principle of microscopic reversibility. We first show that a suitable canonical transformation of the results for Part I[1] leads to a uniformization of all coordinates, with attendant advantages noted below, and leads thereby in a systematic way to an integral expression for the semiclassical S matrix. A symmetrical choice for the transformation makes the expression satisfy the desired principle.

As in other recent work,[1–3a] we employ action-angle variables to describe all coordinates but the radial one.[1] These variables were used many years ago in celestial mechanics and later in old quantum theory. Subsequently, apart from a few isolated applications,[5] they were largely unused in molecular collisions until our work some years ago.[6] One of their advantages is that they provide a more physical description of the actual motions in the system.

A second useful property of these coordinates, especially useful from the semiclassical viewpoint, is the uniformized description they give for the motion of all internal coordinates, including rotational and orbital motion. This uniformization, for a molecule with N vibrational coordinates, permits the use of a single semiclassical term instead of a sum of 2^N terms and, unlike the sum, is valid in all domains and so need not be replaced by Airy functions in certain regions. In a system undergoing collision there are also the orbital, rotational, and radial motions of the collision partners to be considered. The first two are uniformized by the action-angle variables but the radial motion is not, since it does not have an "action-angle" counterpart in the strict sense of the term, just as translational degrees of freedom differ from internal coordinates in that they are not "quantized." The canonical transformation introduced in the present paper uniformizes this radial motion also and so completes the uniformization of all coordinates. In Eq. (4.18) of Part I a uniformized R coordinate ("w_R") was suggested, and the present paper describes the elaboration of that idea.

II. SUMMARY

Some familiarity with either of the two articles in Ref. 1, referred to collectively as Part I, will be supposed for brevity. We recall that in Part I the Schrödinger wavefunction was obtained in semiclassical form by determining its phase and amplitude. The former was found by solving the Hamilton–Jacobi partial differential equation by the method of characteristics. Such a solution involved the integration of Hamilton's equations of motion, the exact classical trajectories being the characteristics. From a knowledge of the initial wavefunction, the initial phase was known as a function of all the coordinates. The increment in phase was then obtained along the trajectories by means of the integration, so yielding the phase of the final wavefunction as a function of all coordinates. The amplitude was obtained from the flux conservation equation. It can also be obtained from the phase using the "van Vleck determinant," as in Sec. V later.

We denote by $\psi_{nE}^{(+)}(wR)$ the semiclassical wavefunction obtained in Part I for a system in the initial quantum state n $(=n_1, \cdots, n_r)$ and energy E. The coordinates are transformed in the next section from $(w_1, \cdots, w_r, R)$ to $(\bar{w}_1, \cdots, \bar{w}_r, \tau)$. Various operations in the present paper are summarized in (2.1)–(2.5), where S_{mn} is an on-the-energy shell S-matrix element for a transition from state n to state m. The w_i are angle

variables and R is a radial coordinate:

$$S_{mn}\delta(E-E') = \langle mE'^{(-)} \mid nE^{(+)}\rangle \tag{2.1}$$

$$= \int \langle mE'^{(-)} \mid wR\rangle dwdR\langle wR \mid nE^{(+)}\rangle \tag{2.2}$$

$$= \int \langle mE'^{(-)} \mid \bar{w}\tau\rangle d\bar{w}d\tau\langle \bar{w}\tau \mid wR\rangle \times dwdR\langle wR \mid nE^{(+)}\rangle \tag{2.3}$$

$$= \int \langle mE'^{(-)} \mid \bar{w}\tau\rangle d\bar{w}d\tau\langle \bar{w}\tau \mid nE^{(+)}\rangle \tag{2.4}$$

$$= \delta(E-E')\int \langle mE^{(-)} \mid \bar{w}\rangle d\bar{w}\langle \bar{w} \mid nE^{(+)}\rangle. \tag{2.5}$$

Equation (2.1) is a standard expression[7] involving outgoing waves ($-$sign) in a state mE' and ingoing waves ($+$sign) in a state nE. Equation (2.2) introduces an identity operator $\int \mid wR\rangle dwdR\langle wR \mid$, as does (2.3). The element $\langle wR \mid nE^{(+)}\rangle$ is $\psi_{nE}{}^{(+)}(wR)$, and has a phase $S(wR, nE)$. Equations (2.1)–(2.2) could not be used in Part I because those semiclassical wavefunctions were not valid near the classical turning point of the R motion. (Instead a method which calculated S_{mn} from wavefunctions at large R was devised.) The transformation element $\langle \bar{w}\tau \mid wR\rangle$ appears later, apart from a preexponential factor, as $\exp[-iG_1(wR, \bar{w}\tau)/\hbar]$. The wavefunction in the $\bar{w}\tau$ representation, $\langle \bar{w}\tau \mid nE^{(+)}\rangle$, is denoted later by $\bar{\psi}_{nE}{}^{(+)}(\bar{w}\tau)$ and has a phase $\bar{S}(\bar{w}\tau, nE)$; $\langle mE'^{(-)} \mid \bar{w}\tau\rangle$ appears as $\bar{\psi}_{mE'}{}^{(-)*}(\bar{w}\tau)$, with a phase $-\bar{S}^{(-)}(\bar{w}\tau, mE')$. Equations (2.4) and (2.5) yield an integral expression which is evaluated in the present article.

In Sec. III the phase of semiclassical wavefunction of Part I $S(wR, nE)$ is given. The method of transforming this wavefunction to one in a new representation $(\bar{w}\tau)$ is described in Sec. IV, together with a specific form which makes τ a time coordinate and makes the $\bar{w}_i$ constants of the motion. The amplitudes of the original and of the transformed wavefunction are given in Sec. V. Time reversal and its consequences for action-angle variables are described in Sec. VI and in detail in Sec. IX. The expression for the S matrix is derived in Sec. VII [Eqs. (7.2)–(7.4)].

Several specific forms of (7.2)–(7.4) are then considered. The first, a "turning-point value representation," (TVR), appropriate for inelastic rather than reactive collisions, is based on one symmetrical form of the transformation and the resulting S_{mn} obeys the principle of microscopic reversibility. Another representation considered is a "final-value representation" (FVR). The resulting S_{mn} is based on an unsymmetrical transformation and does not satisfy microscopic reversibility (a fact which does not eliminate its numerical usefulness). Finally, a symmetrical representation for reactive collisions can also be considered. Apart from several π terms, the FVR is the same as one obtained by Miller[2b] on more heuristic grounds. Only in the stationary phase approximation are the TVR and FVR expressions for S_{mn} equal. The two representations are compared in Sec. VIII. Some concluding comments on the topics of uniformization of coordinates and on invariance properties of Eqs. (7.5)–(7.6) for S_{mn} are made in Sec. X.

III. SEMICLASSICAL WAVEFUNCTION OF PART I

To simplify the notation it will be useful to employ throughout the $\bar{n}_i$'s defined, through their relation to the action variables J_i, by Eq. (4.27) of Ref. 1(b). The $\bar{n}_i h$ can be regarded as momenta p_i, with initial values $n_i h$. They are canonically conjugate to the angle variables w_i.[8] There is also the radial coordinate R.

The wavefunction for the actual system, $\psi_{nE}{}^{(+)}(wR)$ in the wR representation in Part I, is a semiclassical solution of the time-independent Schrödinger equation and is given by

$$\psi_{nE}{}^{(+)}(wR) \underset{R\to\infty}{\sim} (Rv_n{}^{1/2})^{-1} \times \exp[2\pi i\sum_i n_i w_i - ik_n R + \tfrac{1}{2}(in_1\pi)] + (Rv^{1/2})^{-1} \mid \partial w_i/\partial w_j{}^0 \mid^{-1/2} \exp iS(wR, nE)/\hbar, \tag{3.1}$$

where

$$S(wR, nE) = \sum_i \left(\int_{w_i{}^0}^{w_i} \bar{n}_i dw_i + n_i w_i{}^0\right) h + \int_{R_0}^{R} p_R dR + p_R{}^0 R_0 + \tfrac{1}{2}(n_1+1)\pi\hbar, \tag{3.2}$$

as in Eqs. (4.25), (4.26), and (4.17b) of Ref. 1(b). The integrals in (3.2) are evaluated along the actual classical trajectory, from an initial point (w^0R_0) to the turning point of the R motion and thence to the point (wR). n_i and $p_R{}^0$ are the initial values of $\bar{n}_i$ and p_R (the values at w^0R_0). As is clear from the discussion in Part I, Eq. (3.2) also serves to extend the term containing $\exp(-ik_nR)$ in (3.1) to smaller R. Thus, the wavefunction $\psi_{nE}{}^{(+)}(wR)$ is the sum of two terms, each of the form $A\exp iS/\hbar$:

$$\psi_{nE}{}^{(+)}(wR) = \sum A \exp iS(wR, nE)/\hbar. \tag{3.3}$$

Integration of (3.2) by parts yields (3.4), on writing $k\hbar$ for p_R and noting that $p_R{}^0$ is negative and equal to $-k_n\hbar$:

$$\frac{S(wR, nE)}{\hbar} = 2\pi\sum_i \left(\bar{n}_i w_i - \int_{n_i}^{\bar{n}_i} w_i d\bar{n}_i\right) + kR - \int_{-k_n}^{k} Rdk + \tfrac{1}{2}n_1\pi + (\tfrac{1}{2}\pi), \tag{3.4}$$

where the $+\frac{1}{2}\pi$ term is omitted for the ingoing term in (3.3). In (3.4) k denotes $p_R/\hbar$ and so can be positive or negative in the present paper, unlike k_n which is defined as positive. Computation of δS from (3.4)[9] verifies that S is a function only of the arguments

cited ($wRnE$) and that

$$\partial S/\partial w_i=\bar{n}_i h,$$
$$\partial S/\partial R=p_R\equiv k\hbar, \tag{3.5a}$$

and

$$\partial S/\partial n_i=w_i^0 h-(\mu R_0 \nu_i^0/p_R^0)+\tfrac{1}{2}\pi\hbar\delta_{1i},$$
$$\frac{\partial S}{\partial E}=\frac{R^0\mu}{p_R^0}+\int_{R_0}^{R}\left(\frac{\mu}{p_R}\right)dR, \tag{3.5b}$$

where δ_{1i} is the Kronecker delta and ν_i^0 is the initial value of $\partial H/\partial(n_i h)$ at large R. The trajectories along which (3.2) and (3.4) are integrated satisfy Eq. (4.15) of Part I, which are in the form of Hamilton's equations, $dq_i/dt=\partial H/\partial p_i$, $dp_i/dt=-\partial H/\partial q_i$, t in our case being a monotonically increasing parameter (e.g., "time") measuring position along the trajectory. For the present variables these equations in Part I read

$$dw_i/dt=\partial H/\partial(\bar{n}_i h), \qquad dR/dt=\partial H/\partial p_R=p_R$$
$$d(\bar{n}_i h)/dt=-\partial H/\partial w_i, \qquad dp_R/dt=-\partial H/\partial R. \tag{3.6}$$

In performing the integrals over $\bar{n}$ and k in (3.4) it should be noted that these variables do not usually vary monotonically along a trajectory, and so cannot themselves be used as integration variables. Instead a monotonically varying quantity [the t in (3.6)] is introduced and then the relevant integrals become $\int w_i(d\bar{n}_i/dt)\,dt$ and $\int R(dk/dt)\,dt$.

IV. CANONICAL TRANSFORMATION

The angle variables w_i ($i=1$ to r) and radial coordinate R are denoted by q_i ($i=1$ to $r+1$) and the conjugate momenta of the latter by p_i. The new coordinates and momenta are represented by $\bar{q}_i$ and $\bar{p}_i$. We set

$$\bar{q}_i=\bar{w}_i \ (i=1 \text{ to } r), \qquad \bar{q}_{r+1}=\tau, \qquad \bar{p}_{r+1}=E, \tag{4.1}$$

where τ will prove to be the "time" variable since $\bar{p}_{r+1}$ is chosen as E.

We seek a canonical transformation via a generating function $G_2(q,\bar{p})$, the transformation being given by[10]

$$\bar{q}_i=\partial G_2/\partial\bar{p}_i, \qquad p_i=\partial G_2/\partial q_i. \tag{4.2}$$

The generating function G_2 serves to transform the instantaneous variables (w, R) of a trajectory to new variables $(\bar{w},\tau)$, by matching the instantaneous momenta (p_i) to the partial derivatives of G_2. From a knowledge of $(w_1,\cdots,w_r,R,\bar{n}_1,\cdots,\bar{n}_r,p_R)$ it yields a knowledge of $(\bar{w}_1,\cdots,\bar{w}_r,\tau,\bar{p}_1,\cdots,\bar{p}_{r+1})$.

In the $\bar{w}\tau$ representation the wavefunction can be written, except near any possible singularities of $\bar{A}$, as

$$\bar{\psi}_{nE}{}^{(+)}(\bar{w}\tau)=\bar{A}\exp i\bar{S}(\bar{w}\tau,nE)/\hbar, \tag{4.3}$$

where n and E are the initial values of $\bar{n}$ and $\bar{E}$. By the rule of classical canonical transformations, and thereby of semiclassical unitary transformations of the ψ's we may write[11]

$$\bar{S}(\bar{q},p^0)=S(q,p^0)-G_1(q,\bar{q}), \tag{4.4}$$

where

$$G_1(q,\bar{q})=G_2(q,\bar{p})-\sum_{i=1}^{r+1}\bar{q}_i\bar{p}_i \tag{4.5}$$

according to the usual Legendre transformation.[10] Because of (4.2) a differentiation of this expression for $G_1(q,\bar{q})$ with respect to $\bar{p}_i$ shows that $G_1(q,\bar{q})$ is independent of $\bar{p}_i$, as indeed it must be.

We shall employ a G_2 based on exact trajectories. One which we have devised to yield a new convenient set of coordinates can be written as

$$G_2(wR,\bar{n}^T h\,E)=\sum_i\left(\int_{w_i{}^T}^{w_i}\bar{n}_i dw_i+\bar{n}_i{}^T w_i{}^T\right)$$
$$+\int_{R^T}^{R}p_R dR+p_R{}^T R^T, \tag{4.6}$$

where the rhs of (4.6) depends on E implicitly; $w_i{}^T$ and R^T remain to be assigned; $\bar{n}_i{}^T$ and $p_R{}^T$ are the values of $\bar{n}_i$ and p_R at $(w^T R^T)$; and, as the notation on the lhs of (4.6) implies, we have chosen in addition to (4.1),

$$\bar{p}_i=\bar{n}_i{}^T h \qquad (i=1 \text{ to } r). \tag{4.7}$$

G_2 has, from (4.2), the properties that

$$\partial G_2/\partial w_i=\bar{n}_i h, \qquad \partial G_2/\partial R=p_R. \tag{4.8}$$

Differentiation of (4.6) with respect to $\bar{n}_i{}^T h$ and to E, using (4.2), yields the new coordinates $\bar{w}_i$ and τ. Details of the proof are given in Appendix A:

$$\bar{w}_i=\partial G_2/\partial\bar{n}_i{}^T h=w_i{}^T-R^T\mu\nu_i{}^T/p_R{}^T$$
$$(\text{when } p_R{}^T\neq 0) \tag{4.9a}$$
$$\text{or}=w_i{}^T \qquad (\text{when } p_R{}^T\equiv 0), \tag{4.9b}$$
$$\tau=\frac{\partial G_2}{\partial E}=\int_{R^T}^{R}\left(\frac{\mu}{p_R}\right)dR+\frac{\mu R^T}{p_R{}^T}$$
$$(\text{when } p_R{}^T\neq 0) \tag{4.9c}$$
$$\text{or}=\int_{R^T}^{R}\left(\frac{\mu}{p_R}\right)dR$$
$$(\text{when } p_R{}^T\equiv 0). \tag{4.9d}$$

$\nu_i{}^T$ is the partial derivative of H with respect to $\bar{n}_i{}^T h$, holding E, w_i, R, and $\bar{n}_j{}^T$ ($j\neq i$) constant, and is the mechanical frequency of motion of the ith degree of freedom at that point. $d\tau$, calculated from (4.9c) and (4.9d) equals $\mu dR/p_R$ for a given $(p_R{}^T, R^T)$, and so equals the "time increment" dt in (3.6). In (4.9d) τ is thus the time for the system to go from a point $(w^T R^T)$ to the point (wR) along a trajectory.

Equation (4.5) now reads

$$G_1(wR,\bar{w}\tau)=G_2(wR,\bar{n}^T E)-\sum_i\bar{n}_i{}^T\bar{w}_i h-E\tau. \tag{4.10}$$

Actually, one should have replaced the $\bar{n}$, $\bar{n}_i{}^T$, $p_R{}^T$, and E in (4.6) and (4.10) by other symbols (e.g., $\bar{n}^*$, $\bar{n}_i{}^{T*}$, $p_R{}^{T*}$, and energy E^*) and then verify by application of (4.8) that

$$\bar{n}_i{}^*h \equiv \partial G_2/\partial w_i = \partial G_1/\partial w_1 = \partial S(wR, nE)/\partial w_i = \bar{n}_i h$$

$$p_R{}^* \equiv \partial G_2/\partial R = \partial G_1/\partial R = \partial S(wR, nE)/\partial R = p_R, \quad (4.11)$$

and hence that $\bar{n}_i{}^{T*}$ and E^* equal $\bar{n}_i{}^T$ and E. One would again thus obtain (4.6), (4.9), and (4.10).

From (3.4), (4.4), and (4.6) we now may write, finally,

$$\frac{\bar{S}(\bar{w}\tau, nE)}{\hbar} = 2\pi \sum_i \bar{n}_i{}^T \bar{w}_i + \frac{E\tau}{\hbar} - 2\pi \sum_i \int_{n_i}^{\bar{n}_i{}^T} w_i d\bar{n}_i - \int_{k_0}^{k^T} R dk + \tfrac{1}{2} n_1 \pi + (\tfrac{1}{2}\pi), \quad (4.12)$$

where k^T and k_0 are the values of k at $(w^T R^T)$ and $(w^0 R_0)$. The $(\frac{1}{2}\pi)$ is omitted if, at the given point (wR), the system has not reached the turning point of the R motion.

From (4.12) one may verify by differentiation, as in Appendix A, that

$$\partial \bar{S}/\partial \bar{w}_i = \bar{n}_i{}^T h, \qquad \partial \bar{S}/\partial \tau = E. \quad (4.13)$$

One also notes from (4.4) that $\partial \bar{S}/\partial p^0$ equals $\partial S/\partial p^0$ and, hence, from (3.5b), that

$$\partial \bar{S}/\partial n_i = \bar{w}_i{}^0 h + \tfrac{1}{2}\pi\hbar\delta_{1i},$$

$$\frac{\partial \bar{S}}{\partial E} = \int_{R_0}^{R} \left(\frac{\mu}{p_R}\right) dR + \frac{\mu R_0}{p_R{}^0}, \quad (4.14)$$

where

$$\bar{w}_i{}^0 = w_i{}^0 - (\mu v_i{}^0/p_R{}^0). \quad (4.15)$$

Equation (4.14) can also be obtained directly from (4.12), as in Appendix A.

V. SEMICLASSICAL WAVEFUNCTION. AMPLITUDE OF $\bar{\psi}$

The amplitude $\bar{A}$ can be evaluated by the flux conservation argument used in Part I, noting that the volume element is now $d\tau \prod_i d\bar{w}_i$ and that the velocity along the τ coordinate is $\partial \bar{H}(\bar{q}, \bar{p})/\partial E$, by Hamilton's equation since E is conjugate to τ. Since $G_1(q, \bar{q})$ is not explicitly time dependent, $\bar{H}$ equals H, which in turn equals E. Thus, the velocity is $\partial E/\partial E$, i.e., unity. A region enclosed by a family of trajectories (the "characteristics") has a cross section $\prod_i d\bar{w}_i$, and the flux at any $\bar{w}$ is $|\bar{A}|^2 \partial E/\partial E \prod_i d\bar{w}_i$. Since $\bar{w}_i$, defined by (4.9), is constant along a trajectory, conservation of flux shows that A is also constant along the trajectory. To place the normalization of $\bar{A}$ on a similar basis as the "phase space" one described below, we shall set

$$\bar{A} = |\partial \bar{w}_i/\partial w_j{}^0|^{-1/2} h^{-1/2}, \quad (5.1)$$

a result which can also be motivated on different grounds.[12] The phase of $\bar{A}$ can now be chosen by allowing these factors to be complex valued, i.e., by not regarding $|\ |$ as denoting absolute value: only $|\bar{A}|^2$ entered into the above or following derivation. The $\bar{w}_j{}^0$ in (5.1) is defined in (4.15).

It is useful to verify from (4.3), (4.13), and (5.1) that $\bar{\psi}_{nE}{}^{(+)}$ satisfies orthonormality and completeness. We omit subscripts for brevity and first remark that Eq. (5.1) for A can be rewritten, using (4.13)–(4.14),[13,14] in the concise form for an $(r+1)\times(r+1)$ determinant

$$\bar{A} = |\partial^2 \bar{S}/\partial p_0 \partial \bar{q}|^{1/2} h^{-1/2}, \quad (5.2)$$

where $\bar{q}$ denotes the $\bar{w}_i$ and τ, while p_0 denotes the $n_i h$ and E.

Expanding the phase in a Taylor series and retaining only the leading term,[11,15,2a] we have (on omitting for brevity in the remainder of this section the subscripts and the summations over i)

$$\int \bar{\psi}_{p_0}{}^{(+)*}(\bar{q}) \bar{\psi}_{p_0'}{}^{(+)}(\bar{q})\, d\bar{q} = \int |\bar{A}|^2 \exp[i(\partial \bar{S}/\partial p_0)(p_0' - p_0)/\hbar] d\bar{q} \quad (5.3)$$

($d\bar{q}$ denotes $d\tau \prod_i d\bar{w}_i$ and the exponent is a sum of $r+1$ terms). Noting that $|(\partial/\partial \bar{q})(\partial \bar{S}/\partial p_0)|\, d\bar{q}$ equals $d(\partial \bar{S}/\partial p_0)$ in this $(r+1)$-dimensional space, (5.2) and (5.3) lead to

$$\int \bar{\psi}_{p_0'}{}^{(+)*}(\bar{q}) \bar{\psi}_{p_0}{}^{(+)}(\bar{q})\, d\bar{q} = \delta(p_0 - p_0')/h^r \equiv \delta(E - E') \prod_i \delta(n_i - n_i'). \quad (5.4)$$

Normalization to $\prod_i \delta(n_i - n_i')$ becomes a normalization to $\prod_i \delta_{n_i n_i'}$, when discrete n_i's are employed.

Again, since dp_0 denotes $dE \prod_i d(n_i h)$,

$$\int \bar{\psi}_{p_0}{}^{(+)*}(\bar{q}) \bar{\psi}_{p_0}{}^{(+)}(\bar{q}')\, dE \prod_i dn_i = \int |\bar{A}|^2 h^{-r} \exp[i(\partial \bar{S}/\partial \bar{q})(\bar{q}' - \bar{q})/\hbar] dp_0. \quad (5.5)$$

Since $|\partial/\partial p_0 (\partial \bar{S}/\partial \bar{q})|\, dp_0$ equals $d(\partial \bar{S}/\partial \bar{q})$, Eq. (5.2) for $\bar{A}$ converts this equation to the completeness relation,

$$\int \bar{\psi}_{p_0}{}^{(+)*}(\bar{q}) \bar{\psi}_{p_0}{}^{(+)}(\bar{q}')\, dE \prod_i dn_i = \delta(\bar{q} - \bar{q}') \equiv \delta(\tau - \tau') \prod_i \delta(\bar{w}_i - \bar{w}_i'). \quad (5.6)$$

VI. TIME-REVERSED WAVEFUNCTION

In the state described by the wavefunction $\bar{\psi}_{nE}{}^{(+)}(\bar{w}\tau)$, the system consists of an ingoing partial wave in state n and of outgoing partial waves in various states $\bar{n}$, as in Fig. 1. The time-reversed state $\bar{\psi}_{mE'}{}^{(-)}(\bar{w}\tau)$ needed for the evaluation of S_{mn} via Eq. (2.1), consists of ingoing partial waves in various states $\bar{m}$ and of an outgoing wave in state m (Fig. 1).

A time-reversal operator changes the sign of all

conventional momenta $(p_x, p_R, \cdots)$, leaves unchanged the sign of all conventional position coordinates, and so changes the sign of angular momenta $(\mathbf{r}\times\mathbf{p})$.[16] Since action-angle variables arise from canonical transformations, which frequently mix conventional momenta and coordinates, the time-reversal behavior of each $(m_i h, w_i)$ pair needs to be studied individually, and we describe this behavior later in Sec. VIII, to avoid a lengthy digression at this point.

We may write microscopic reversibility in the form[17]

$$S_{mn}=S_{n'm'}, \tag{6.1}$$

where the primes designate properties for the time-reversed system, the prime bearing no relation to that in E', of course. It can be shown, as in Sec. VIII,[16] that

$$\bar{\psi}_{mE'}{}^{(-)}(\bar{w}\tau)=K\bar{\psi}_{m'E'}{}^{(+)}(\bar{w}\tau), \tag{6.2}$$

where K denotes the time-reversal operator. Using this result and Eq. (4.12) the arguments in VIII show that

$$\bar{\psi}_{mE'}{}^{(-)}(\bar{w}\tau)=\bar{A}^{(-)}\exp i\bar{S}^{(-)}/\hbar, \tag{6.3}$$

where

$$\frac{\bar{S}^{(-)}(mE',w\tau)}{\hbar}=2\pi\sum_i\left(\bar{m}_i{}^T\bar{w}_i-\int_{m_i}^{\bar{m}_i{}^T}w_i d\bar{m}_i\right)+\frac{E'\tau}{\hbar}-\int_{k^0(m)}^{k^T}Rdk-\tfrac{1}{2}m_1\pi-(\tfrac{1}{2}\pi). \tag{6.4}$$

The w_i's appearing in (6.4) are such that the $\bar{w}_i$ for each time-reversed m trajectory equals that for an n trajectory. The $k^0(m)$ in (6.4) is k_m, rather than $-k_m$, since it is the value at (w^0R_0) of k for this time-reversed system.

The amplitude $\bar{A}^{(-)}$ in (6.3) is, from Sec. VIII and in (5.1), given by

$$\bar{A}^{(-)*}=|\,\partial\bar{w}_i/\partial\bar{w}_j{}^0\,|^{-1/2}\hbar^{-1/2}, \tag{6.5}$$

the $\bar{w}$'s referring, of course, to the m trajectory. Relations analogous to (4.13)–(4.14) are obeyed, but with

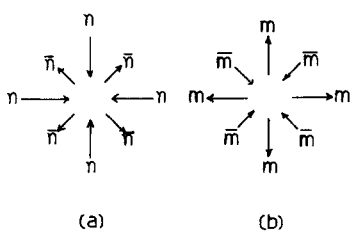

FIG. 1. (a) Pictorial description of $\bar{\psi}_{nE}{}^{(+)}$. Lines represent partial wave ingoing in state n and partial waves outgoing in state $\bar{n}$. (b) Pictorial description of time-reversed wavefunction $\bar{\psi}_{mE}{}^{(-)}$. Lines represent partial waves ingoing in state $\bar{m}$ and partial wave outgoing in state m.

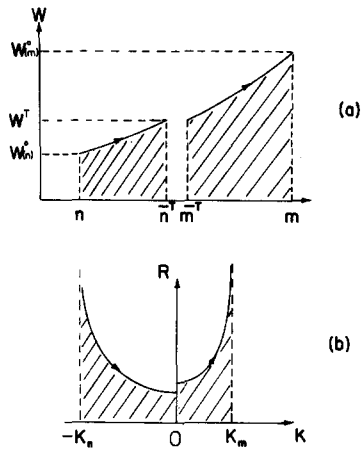

FIG. 2. (a) Plot of w vs $\bar{n}$ for n trajectory and $\bar{w}$ vs $\bar{m}$ for m trajectory. Shaded areas describe m and n integrals in Eq. (7.3) for TVR.[18] (b) Plot of R vs k for n trajectory and for m trajectory. Shaded areas describe k integrals in Eq. (7.3) for TVR.

$\bar{S}$, n's, E's, and $\bar{n}^T$'s replaced by $\bar{S}^{(-)}$, m's, E''s, and $\bar{m}^T$'s.

VII. S MATRIX

On introducing (4.3) and (6.3) into (2.4), S_{mn} is

$$S_{mn}\delta(E-E')=\int\bar{A}A^{(-)*}\exp(i/\hbar)[\bar{S}(\bar{w}\tau,nE)-\bar{S}^{(-)}(\bar{w}\tau,mE')]d\tau\prod_i d\bar{w}_i. \tag{7.1}$$

The only term depending on τ in the integrand is $\exp i(E-E')\tau/\hbar$. Integration over τ yields a delta function $\delta(E-E')$. Thus,

$$S_{mn}=h\int\bar{A}\bar{A}^{(-)*}(\exp i\Delta)\prod_i d\bar{w}_i, \tag{7.2}$$

where from (4.12) and (6.4)

$$\Delta=2\pi\sum_i\left[(\bar{n}_i{}^T-\bar{m}_i{}^T)\bar{w}_i-\int_{n_i}^{\bar{n}_i{}^T}w_i d\bar{n}_i-\int_{\bar{m}_i{}^T}^{m_i}w_i d\bar{m}_i\right]-\int_{k^0(n)}^{k^T(n)}Rdk-\int_{k^T(m)}^{k^0(m)}Rdk+\tfrac{1}{2}(n_1+m_1+1)\pi, \tag{7.3}$$

and from (5.1) and (6.5)

$$h\bar{A}\bar{A}^{(-)*}=|\,\partial\bar{w}_i/\partial\bar{w}_j{}^0(n)\,|^{-1/2}\,|\,\partial\bar{w}_i/\partial\bar{w}_j{}^0(m)\,|^{-1/2}. \tag{7.4}$$

Here, the (n) and (m) emphasize that the properties are those of m and n trajectories; $k^0(n)$ and $k^0(m)$ equal $-k_n$ and $+k_m$, respectively.

Specific representations of (7.2)–(7.4) are obtained by choosing R^T. The first representation we consider is one appropriate to inelastic collisions: We let R^T denote the turning point of the R motion.

In this turning-point value representation (TVR), Eq. (4.9b) shows, $\bar{w}$ equals w^T, the value of w at the turning point. Since $\bar{w}$ is the same for the n and m trajectories in (7.3), w^T is also and, hence, in a plot containing m and n trajectories as in Fig. 2(a), w itself varies continuously from $w^0(n)$ to $w^0(m)$. The sum of a pair of m and n integrals in (7.3) might be represented in area in a typical case by the shaded re-

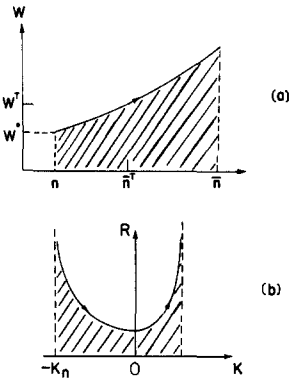

FIG. 3. (a) Plot of w vs $\bar{n}$ for a complete n trajectory. Shaded area describes n integral in Eq. (7.8) for FVR.[18] (b) Plot of R vs k for a complete m trajectory. Shaded area describes k integral in Eq. (7.8) for FVR.

gions in Fig. 2(a).[18] The pair of k integrals in (7.3) might be similarly represented by the shaded area in Fig. 2(b). There can be a sizeable discontinuity in $\bar{m}$ and R (i.e., in $\bar{m}^T-\bar{n}^T$ and in R^T) in Figs. 2(a) and 2(b), as indicated, as in any "Fourier analysis." [S_{mn} can be regarded as a Fourier coefficient in an expansion of $\psi_{nE}{}^{(+)}(\bar{w}\tau)$ in terms of a complete set of $\psi_{mE'}{}^{(-)}(\bar{w}\tau)$'s.][19]

To underline the Fourier component nature of S_{mn} one can rewrite (7.3) as

$$\Delta=2\pi\sum_i\left[(n_i-m_i)\bar{w}_i-\int_{n_i}^{\bar{n}_i{}^T}(w_i-\bar{w}_i)\,d\bar{n}_i-\int_{\bar{m}_i{}^T}^{m_i}(w_i-\bar{w}_i)\,d\bar{n}_i\right]-\int_{-k_n}^{k(n)}Rdk-\int_{k(m)}^{k_m}Rdk+\tfrac{1}{2}(n_1+m_1+1)\pi, \quad (7.5)$$

where $k(n)$ and $k(m)$ denote the values of k at (w^TR^T) and are zero in the TVR. Equation (7.2) may also be written explicitly for later reference as

$$S_{mn}=\int_0^1\left|\frac{\partial\bar{w}_i}{\partial\bar{w}_j{}^0(n)}\right|^{-1/2}\left|\frac{\partial\bar{w}_i}{\partial\bar{w}_j{}^0(m)}\right|^{-1/2}\exp i\Delta\prod_i d\bar{w}_i, \quad (7.6)$$

where in the TVR, $\bar{w}_i$ is $w_i{}^T$. In (7.5) Δ can be regarded as the sum of two terms: $2\pi\sum(n_i-m_i)\bar{w}_i$ and the remaining portion of Δ. The Fourier component nature of (7.6) is thus clear. When $|S_{mn}|^2$ is very small for large $|m-n|$, it usually is so because of large oscillations in the integrand due to the $2\pi(n-m)\bar{w}$ term, not compensated by oscillations in the remaining factor when the latter is slowly varying with $\bar{w}$.

The integrals in Figs. 2(a) and 2(b) for the m half of the trajectories have the values they would have if one integrated an m trajectory beginning at (w^TR^T), with $\bar{m}=\bar{m}^T$ and $k=k(m)$ and ending at $w^0(m)$ and an R_0, and with $\bar{m}=m$ and $k=k_m$. (The results for $|S_{mn}|^2$ are independent of this R_0.) From a numerical integration point of view one doesn't know in advance the $\bar{m}^T$, w^T, and R^T with which to begin the integration in the m part of the trajectory in Figs. 2(a) and 2(b). However, one can perform the integration by starting at the right end (i.e., at m and k_m) and integrating Hamilton's equations backwards in time, i.e., using Eqs. (3.6) with dt replaced by $-dt$. Another method can also be derived for obtaining these m-trajectory integrals.[20]

A second representation would be one where R^T is chosen to be a large R and where $p_R{}^T$ is chosen to be positive. In this case, the (w^TR^T) are points at large R on the outgoing arm of the n trajectories and on the incoming arm of the m trajectories. Thus, here $\bar{m}_i{}^T$ and $k(m)$ equal their values in this region, m_i and k_m. The integrals over $d\bar{m}$ and $dk(m)$ in (7.3) then vanish and $\bar{A}^{(-)}$ becomes unity. Equations (7.2)–(7.4) now become

$$S_{mn}=\int|\partial\bar{w}_i/\partial\bar{w}_j{}^0|^{-1/2}\exp i\Delta\prod_i d\bar{w}_i, \quad (7.7)$$

where $\bar{w}$ is given by (4.9a), in which $p_R{}^T$ is the final value of p_R for this particular n trajectory; Δ is

$$\Delta=2\pi\sum_i(\bar{n}_i-m_i)\bar{w}_i-\int_{n_i}^{\bar{n}_i}w_i d\bar{n}_i-\int_{-k_n}^{k}Rdk+\tfrac{1}{2}(n_1+m_1+1)\pi. \quad (7.8)$$

This equation for S_{mn} no longer obeys the principle of microscopic reversibility, unlike (7.5)–(7.6) in the TVR. The difference in this respect is due to the fact that the semiclassical unitary transformation is unsymmetrical when R^T is chosen to be at the end of an arm of a trajectory rather than at its turning point. In fact, as one sees by setting $\bar{m}^T$ and k^T in (6.4) equal to m and k_m and setting $\bar{n}^T$ and k^T in (4.12) equal to a final $\bar{n}$ and to a final k, this transformation serves to transform $\psi_{mE'}{}^{(-)}(wR)$ to $\bar{\psi}_{mE'}{}^0(\bar{w}\tau)$ and $\bar{\psi}_{nE}{}^{(+)}(wR)$ to some final $\bar{\psi}_{nE}{}^{(+)}(\bar{w}\tau)$, thus giving rise to an asymmetry. For later comparison the $\bar{n}$ and k integrals in (7.8) are sketched in Figs. 3(a) and 3(b).

In the case of reactive collisions, the second representation is still meaningful,[21] but the first is not since there is no "turning point" in this case. For this situation one can also elect another symmetrical representation, with the aid of conventional coordinates. We intend to consider the topic in a later communication.

Apart from the π terms Eqs. (7.7)–(7.8) for the FVR have been given by Miller, who used a different approach.[2b] In the available tests of (7.7)–(7.8), its accuracy has been reasonable, though becoming poor at low transition probabilities. Large deviations from microscopic reversibility also begin to occur there. To be sure, the fact that expressions, such as those in the TVR for inelastic collisions, satisfy microscopic reversibility by no means ensures their accuracy.

One can attempt to improve the FVR in this respect by setting

$$S_{mn}=\tfrac{1}{2}(S_{mn}+S_{n'm'})=\tfrac{1}{2}S_{mn}{}^{\mathrm{FVR}}+\tfrac{1}{2}S_{n'm'}{}^{\mathrm{FVR}}, \quad (7.9)$$

where the first half of the equation is exact and where the FVR superscript denotes the FVR approximation. This modified FVR satisfies microscopic reversibility and some tests of it have been reported elsewhere.[22] It will be interesting to compare the relative accuracy of the TVR and of this modified FVR.

VIII. COMPARISON OF TWO REPRESENTATIONS

We have already noted that the turning-point value representation (TVR) obeys microscopic reversibility while the final-value representation (FVR) does not, and we have noted the reason. It is instructive, nevertheless, to compare the two representations more closely and see how they agree in their stationary phase approximation.

To this end we first rewrite their pre-exponential factors as follows: Noting that $\bar{w}_i$ equals $w_i{}^T$ in TVR and using the rules for multiplication of determinants and for relating volume elements by Jacobians, we have from (7.4)

$$h\bar{A}\bar{A}^{(-)*}\prod_i d\bar{w}_i$$
$$= |\,\partial w_i{}^T/\partial\bar{w}_j{}^0(n)\,|^{-1/2}\,|\,\partial w_i{}^T/\partial\bar{w}_j{}^0(m)\,|^{-1/2}\prod_i dw_i{}^T$$
$$= |\,\partial\bar{w}_i{}^0(m)/\partial\bar{w}_j{}^0(n)\,|^{-1/2}\prod_i d\bar{w}_i{}^0(m) \quad \text{(TVR)}. \quad (8.1)$$

For the final value representation we have, instead,

$$h\bar{A}\bar{A}^{(-)*}\prod_i d\bar{w}_i = |\,\partial\bar{w}_i/\partial\bar{w}_j{}^0(n)\,|^{-1/2}\prod_i d\bar{w}_i \quad \text{(FVR)}. \quad (8.2)$$

It is useful to compare the two representations using the stationary phase approximation. The point of stationary phase of the integral (7.2) for S_{mn} occurs at

$$\partial\Delta/\partial\bar{w}=0, \quad (8.3a)$$

that is, at

$$\bar{m}^T=\bar{n}^T. \quad (8.3b)$$

In the TV representation this equation states that the $\bar{m}^T$ and $\bar{n}^T$ are equal at the R turning point, for those trajectories (a discrete number) satisfying the stationary phase condition. In the FV representation the equation means that the final value of $\bar{n}$ equals m, for the trajectories satisfying the stationary phase condition. One may then verify using the methods in Part I or Part II that the values of the integral for S_{mn} are identical for TVR and FVR, when calculated in the stationary phase approximation.

The relation of the two representations can also be seen by comparing Figs. 2 and 3 and comparing the pre-exponential factors (8.1)–(8.2), for trajectories satisfying the stationary phase condition (8.3). In the TVR this condition means that there is no discontinuity in $\bar{n}^T$ or in R^T, i.e., the n trajectory continues smoothly onto the m trajectory. Δ consists now only of the integrals in (7.3) and the π terms. In the FVR the condition (8.3) means that the final $\bar{n}$ equals m and thus that Figs. 3(a) and 3(b) become identical with Figs. 2(a) and 2(b). The Δ in (7.8) now consists only of the integrals and the π terms and becomes equal to that in (7.3). The pre-exponential factors (8.1) and (8.2) also now become equal. In summary, when the most important trajectories contributing to the integral for S_{mn} are in a neighborhood of the discrete number of trajectories satisfying the stationary phase condition (8.3), the two representations become equivalent.

In the case of classically inaccessible trajectories, it may be noted the stationary phase condition (8.3) is not satisfied by any real-valued trajectory. Instead, by analytic continuation one finds the complex-valued trajectories (in several-dimensional complex variable space) which satisfy (8.3) and then evaluates the integral by analytic continuation (in principle at least) or by the stationary phase method in Part I or II.

IX. TIME REVERSAL IN DETAIL

We consider the time-reversal operation at greater length in the present section.

Let $\psi_{nE}{}^0(Q)$ denote an unperturbed wavefunction in any representation Q. It is convenient to define the time-reversal operator K with the aid of ψ^0 [16]:

$$K\psi_{nE}{}^0(Q)=\psi_{n'E}{}^0(Q), \quad (9.1)$$

where n' designates the time-reversed state, i.e., the state where all momenta, angular momenta, and spins are reversed from their values in state n. Usually a phase factor of magnitude unity is present on the right, but for simplicity of notation we adopt (by suitable choice of the phase of ψ^0) a phase convention which makes it unity. K, an antiunitary operator, also has the property that it converts all constants to their complex conjugates, and K^2 equals the identity operator.

The wavefunctions $\psi_{nE}{}^{(\pm)}(Q)$ are given by[16]

$$\psi_{nE}{}^{(\pm)}(Q)=[1+(E-H\pm i\epsilon)^{-1}V]\psi_{nE}{}^0(Q), \quad (9.2)$$

where V is the perturbation (in the given channel) and ϵ is an infinitesimal positive quantity which is made to vanish only after the integral operation implied in the integral operator $(E-H\pm i\epsilon)^{-1}$ has been performed. (Previously we had placed a bar over the $\psi^{(\pm)}$'s when the representation was $\bar{w}\tau$, and we return to this practice later in this section.)

Application of K to (9.2) and insertion of the identity operator $K^{-1}K$ yield[16]

$$K\psi_{nE}{}^{(+)}(Q)$$
$$=K[1+(E-H\pm i\epsilon)^{-1}V]K^{-1}K\psi_{nE}{}^0(Q)$$
$$=[1+(E-H\mp i\epsilon)^{-1}V]\psi_{n'E}{}^0(Q)=\psi_{n'E}{}^{(\mp)}(Q) \quad (9.3)$$

for H's and V's invariant to the time-reversal operator,

Thus, on replacing n and E by m' and E' in (9.3).

we may calculate $\psi_{mE'}{}^{(-)}(Q)$ from

$$\psi_{mE'}{}^{(-)}(Q)=K\psi_{m'E'}{}^{(+)}(Q). \tag{9.4}$$

The antiunitary property of K makes $\langle\psi_1\,|\,\psi_2\rangle$ equal to $\langle K\psi_2\,|\,K\psi_1\rangle$, for any scalar product.[16] Using (9.4), Eq. (2.1) immediately leads to the principle of microscopic reversibility (6.1).

In the wR representation $\psi_{nE}{}^0(Q)$ is of the form

$$\psi_{nE}{}^0(wR)=f_n(R)\prod_{j=1}^{r}\exp(2\pi i n_j w_j), \tag{9.5}$$

where $f_n(R)$ is real. Away from the R turning point $f_n(R)$ is a sinusoidal function of kR but near that point is an Airy function. The $f_n(R)$ is unaffected by the operator K.

To investigate the time reversal it will be convenient to divide the w variables into two classes. In the first class the canonically conjugate variable, action,[23] may be positive or negative. In the second class the action is always positive.

An example of a class I w is the angle conjugate to the z component of angular momentum. (This is the angle between a space-fixed x axis and the line of intersection of the instantaneous rotational plane and the space-fixed xy plane.)[24] Class I w's are unchanged by time reversal, just as conventional Cartesian coordinates are unchanged, but the sign of the n's is changed (e.g., time reversal means reversal of the angular momentum vector). This sign change in an n_i converts the corresponding factor in the wavefunction $\exp 2\pi i n w$ in (9.7) to its complex conjugate, so the operator K in (9.1) for these variables amounts to complex conjugation.

An example of a class II w variable is that describing a vibrational motion. Another is the w conjugate to the total angular momentum. To illustrate the nature of time reversal in this case it is useful to consider the harmonic oscillator. In dimensionless units the action-angle variables for this degree of freedom can be defined by[25]

$$x=(2n+1)^{1/2}\cos 2\pi w, \qquad p_x=(2n+1)^{1/2}\sin 2\pi w, \tag{9.6}$$

where $2n+1$ is always positive. With this choice, a time reversal ($x\rightarrow x$, $p_x\rightarrow -p_x$) implies

$$w\rightarrow -w, \qquad n\rightarrow n. \tag{9.7}$$

This time reversal causes the wavefunction $\exp 2\pi i n w$ to be transformed to its complex conjugate and so, for this choice of w, the operator K in (9.1) again amounts to complex conjugation.

We turn now to the $\bar{w}r$ representation. Here, the unperturbed wavefunction is now completely complex valued:

$$\bar{\psi}_{nE}{}^0(\bar{w}r)=\left[h^{-1/2}\exp\left(\frac{iEr}{\hbar}\right)\right]\prod_{j=1}^{r}\exp(2\pi i\bar{w}_j n_j). \tag{9.8}$$

[The first factor is normalized to $\delta(E-E')$.] The variable $\bar{w}$ is merely a constant for the trajectory (e.g., w at the R turning point) and the previous remarks regarding the two classes of action-angle pairs apply to $\bar{w}$ and need not be repeated. The r in (9.8) is changed to $-r$ by the time-reversal operator K, and so K again is the same as complex conjugation.

According to (9.4), $\psi_{mE'}{}^{(-)}(Q)$ can be obtained by first time-reversing all the degrees of freedom (as implied by the m' on the rhs) and then applying the operator K. Considering the terms in (4.12) in the order given (with $n, \bar{n}^T, \bar{n}, E$ replaced by $m, \bar{n}^T, \bar{m}, E'$), we thus find: The $\bar{m}^T\bar{w}$ and $E'r$ are changed by the prime to $-\bar{m}^T\bar{w}$ and $-E'r$ and then by the K in (9.4) back to $\bar{m}^T\bar{w}$ and $E'r$. We omit the next two integrals for the moment. The final term, which appears as $+\frac{1}{2}n_1\pi i+(\frac{1}{2}\pi)i$ in the exponent of $\psi_{mE'}{}^{(+)}$, is unaffected by the prime in (9.4) but is changed to its complex conjugate by the K operator. If the two integrals are regarded as constants[26] they are similarly affected. Thus, Eq. (6.4) for $\bar{S}^{(-)}$ follows.

Another view of the two integrals, leading to the same result, is the following: The $\bar{m}$ and k integrals in the exponent for $\psi_{m'E'}{}^{(+)}$ begin with integrands w^T and R^T and read, when one includes the i's,

$$-2\pi i\int_{\bar{m}^T}^{m} w\,d\bar{m}-i\int_0^{k_m} R\,dk.$$

$\psi_{mE'}{}^{(-)}$ is obtained in (9.4) by applying K to $\psi_{m'E'}{}^{(+)}$ and so converts these integrals to their complex conjugates

$$2\pi i\int_{\bar{m}^T}^{m} w\,d\bar{m}+i\int_0^{k_m} R\,dk,$$

and thus yields the pair of integrals in (6.4).

Regarding the amplitude $\bar{A}^{(-)}$, the amplitude $\bar{A}^{(+)}$ of $\psi_{mE}{}^{(+)}$ is $|\,\partial\bar{w}_i/\partial\bar{w}_j{}^0\,|^{-1/2}h^{-1/2}$ and is unaffected by the prime operation (e.g., $\bar{w}_i$ and $\bar{w}_j{}^0$ are constant along a trajectory and the prime operation would at most change the sign of each). Application of the operator K as in (9.4) then converts this factor to its complex conjugate and thus yields (6.5).

X. CONCLUDING REMARKS

In this concluding section we comment first on the uniformization of coordinates, and then on some invariance properties of S_{mn}.

Uniformization leads to a removal of any singularities in the simple exponential semiclassical wavefunction by transformation to suitable coordinates. These singularities arise, it will be recalled, because of the presence of $p^{-1/2}$ terms [e.g., the $v^{-1/2}$ in (3.1)] in the pre-exponential factor, p being the momentum. This factor becomes infinite at $p=0$, i.e., at a classical turning point. Examples of this behavior are given in several figures in a recent article,[22] where trajectories are plotted for various sets of coordinates.

Intersection of adjacent trajectories means zero cross-sectional area between them and, hence, for flux conservation, infinite amplitude of the simple exponential semiclassical wavefunction.

Using conventional coordinates there were numerous intersections in the problem examined (linear collision of an atom and an oscillator) for a given number of trajectories.[22] When wR coordinates were used instead, with the same number of trajectories, there were many fewer intersections.[22] Those that remained were largely in the vicinity of the R turning point and there were a few at large R. It was the latter set, the intersections at large R, which necessitated that the integral expression in Part I be evaluated by an asymptotic method (stationary phase), as in Part I or II. When the coordinates $\bar{w}\tau$ were used (either those in the present paper or those in a companion paper) there were no intersections.[22] Their absence permits the integral in the present paper to be evaluated both by asymptotic and nonasymptotic methods. The question arises as to whether the uniformization of the coordinates is complete, that is, whether the relevant pre-exponential factors are nowhere infinite. When the distortion of the angle variables from their unperturbed motion is unusually great it is possible that a singularity of the pre-exponential factor in (7.5) could develop. Thus far we have not yet uncovered one, but the comparison of (7.5)–(7.6) with exact quantum mechanical results has just begun in this laboratory.

It is instructive to examine (7.5)–(7.6) in the TVR with respect to some invariance properties. In the TVR we set $\bar{w}_i=\bar{w}_i{}^T$ and $k(m)=k(n)=0$ in (7.5)–(7.6). The angle variables are multivalued functions of the conventional coordinates and momenta: each w_i is undetermined to an additive integer in that transformation. Thus, when w_i (and hence $w_i{}^T$) is changed in (7.5)–(7.6) by an integer one would expect S_{mn} to be unchanged. Such is indeed the case: $\bar{m}^T$ and $\bar{n}^T$ are unaffected; the integrals over $\bar{n}$ and $\bar{m}$ are also unaffected since $w_i-w_i{}^T$ is unchanged; the $2\pi(n_i-m_i)w_i{}^T$ is changed by an amount $2\pi(n_i-m_i)N$, where N is an integer. Since $\exp[2\pi i(n_i-m_i)N]$ is unity, and since the derivatives in (7.6) are unchanged S_{mn} is also. In fact, if only the w and w^T associated with the m trajectory were changed by an integer S_{mn} would again be unaltered.

We next consider microscopic reversibility. $S_{n'm'}$ can be obtained from (7.5)–(7.6) by interchanging all $\bar{m}$'s and $\bar{n}$'s (including m's and n's and $\bar{m}^T$'s and $\bar{n}^T$'s) and adding primes to all quantities (including w's) to indicate the prime operation. For example, instead of the first term in (7.5) we shall have (omitting the i subscripts and the summation) $2\pi(m'-n')w'^T$ in the TVR. Regardless of whether the angle variable is of class I or II, this term equals, with our previous choice for w's, $-2\pi(m^T-n^T)w^T$, i.e., $2\pi(n^T-m^T)w^T$, and so is the same as the corresponding term in (7.5). The sum of k integrals in (7.5) is changed to the time-reversed value (with m and n trajectories interchanged)

$$-\int_0^{k_m} Rdk-\int_{-k_n}^{0} Rdk,$$

which is the same as the expression in (7.5). The $\bar{n}$ and $\bar{m}$ integrals, with their negative signs, in (7.5) are changed to

$$-\int_{m_i'}^{\bar{m}_i{}'^T}(w_i'-w_i{}'^T)\,d\bar{m}_i-\int_{\bar{n}_i{}'^T}^{n_i}(w_1'-w_i{}'^T)\,d\bar{n}_i.$$

For class II variables this expression equals

$$+\int_{m_i}^{\bar{m}_i{}^T}(w_i-w_i{}^T)\,d\bar{m}_i+\int_{\bar{n}_i{}^T}^{n_i}(w_i-w_i{}^T)\,d\bar{n}_i,$$

which, on interchanging the upper and lower limits and multiplying by a compensating (-1), yields the same result as in (7.5). A similar remark applies, using a modified reasoning, to class I w variables, and to the calculation of the derivatives in (7.6). Thus, (7.5)–(7.6) in the TVR obey microscopic reversibility.

APPENDIX A: DERIVATIVES OF G_2 AND $\bar{S}$ IN SEC. IV

In Eq. (4.6) G_2 depends on E via the integrand p_R and via $p_R{}^T$:

$$p_R=\pm[2\mu(E-H')]^{1/2}, \tag{A1}$$

where H' denotes all the terms in H apart from $p_R{}^2/2\mu$. The sign in (A1) depends on whether (wR) is on the ingoing or the outgoing arm of the trajectory. Taking variations of (4.6) one obtains

$$\delta G_2=\sum_i(\bar{n}_i\delta w_i+w_i{}^T\delta\bar{n}_i{}^T)h+p_R\delta R+R^T\delta p_R{}^T+\int_{R^T}^{R}\delta p_R dR, \tag{A2}$$

where

$$\int_{R^T}^{R}\delta p_R dR=\left[\int_{R^T}^{R}\left(\frac{\mu}{p_R}\right)dR\right]\delta E \tag{A3}$$

and

$$\delta p_R{}^T=(\mu/p_R{}^T)\delta E-\sum_i(\mu\nu_i{}^T/p_R{}^T)\delta\bar{n}_i{}^T h \qquad (\text{if } p_R{}^T\neq 0) \tag{A4a}$$

or

$$\delta p_R{}^T=0 \qquad (\text{if } p_R{}^T\equiv 0). \tag{A4b}$$

In these equations $\nu_i{}^T$ is $\partial H'/\partial(\bar{n}_i{}^T h)$, i.e., $\partial H/\partial(\bar{n}_i{}^T h)$, the mechanical frequency for the ith degree of freedom, evaluated at R^T.

Equations (4.8) and (4.9) in the text follow from these equations.

Turning next to $\bar{S}(\bar{w}\tau, nE)$ given by (4.12) and

computing $\delta\bar{S}$, after first integrating the k integral by parts, we have

$$\delta\bar{S}=\sum_i\left[(\bar{w}_i-w_i^T)\delta\bar{n}_i^T+w_i^0\delta n_i+\bar{n}_i^T\delta\bar{w}_i\right]h+E\delta\tau+\tau\delta E$$

$$-R^T\delta p_R^T+R_0\delta p_R^0+\int_{R_0}^{R^T}\delta p_R dR+\tfrac{1}{2}\pi\hbar\delta n_1. \quad \text{(A5)}$$

The equation for δp_R^0 is the same as (A4a) with T superscripts replaced by ^{0} ones and with $\delta\bar{n}_i^T$ replaced by δn_i. Introduction of (4.9) and (A3)–(A4), with R in (A3) set equal to R_0, yields

$$\delta\bar{S}=\sum_i\left\{\left[w_i^0-(\mu v_i^0/p_R^0)\right]\delta n_i+n_i^T\delta\bar{w}_i\right\}h+E\delta\tau$$

$$+\tfrac{1}{2}\pi\hbar\delta n_1+\left(\int_{R_0}^{R}\frac{\mu dR}{p_R}+\frac{\mu R_0}{p_R^0}\right)\delta E. \quad \text{(A6)}$$

The coefficients of δn_i, $\delta\tau$, $\delta\bar{w}_i$, and δE give the corresponding derivatives of $\bar{S}$ in (4.13)–(4.14).

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[1] Part I refers to the following two articles (a) and (b), (a) being a summary of (and introduction to) (b). (a) R. A. Marcus, Chem. Phys. Letters **7,** 525 (1970); cf. *Proceedings of the Conference on Potential Energy Surfaces in Chemistry.* Aug. 10–13, 1970, University of California, Santa Cruz, Calif., edited by W. A. Lester (IBM Res. Lab., San Jose, Calif., 1971), p. 58. (b) J. Chem. Phys. **54,** 3965 (1971). In Eq. (6.6′), for Δ read $\hbar\Delta$; in Eq. (7.16), for $(w-w_i')$ $(w-w_j')$, read (w_i-w_i') (w_j-w_j').

[2] (a) W. H. Miller, J. Chem. Phys. **53,** 1949 (1970); (b) **53,** 3578 (1970); (c) **54,** 5386 (1971); (d) Chem. Phys. Letters **7,** 431 (1970); (e) Acct. Chem. Res. **4,** 161 (1971).

[3] Other examples of recent semiclassical work include: (a) R. D. Levine and B. R. Johnson, Chem. Phys. Letters **7,** 404 (1970); **8,** 501 (1971); (b) P. Pechukas, Phys. Rev. **181,** 166, 174 (1969); (c) I. L. Beigman, L. A. Varnshtein and I. I. Sobel'man. Zh. Eksp. Teor. Fiz. **57,** 1703 (1969) [Sov. Phys. JETP **30,** 920 (1970)]; (d) I. C. Percival and D. Richards, J. Phys. **B3,** 315, 1035 (1970).

[4] J. N. L. Connor and R. A. Marcus, J. Chem. Phys. **55,** 5636 (1971).

[5] See, e.g., J. Light, J. Chem. Phys. **36,** 1016 (1962).

[6] R. A. Marcus, J. Chem. Phys. **45,** 4500 (1966); **49,** 2617 (1968); A. O. Cohen and R. A. Marcus, *ibid.* **49,** 4509 (1968); **52,** 393 (1970); S. F. Wu and R. A. Marcus, *ibid.* **53,** 4026 (1970).

[7] M. L. Goldberger and K. M. Watson, *Collision Theory* (Wiley, New York, 1964), p. 193, of which the present (2.1) is an on-the-energy-shell example.

[8] In terms of satisfying Hamilton's equations, both $\bar{n}_i h$ and the $(\bar{n}_i+\delta_i)h$ in Ref. 1 are canonically conjugate to w_i. In terms of properties involving a generating function G_2 (e.g., $p_i=\partial G_2/\partial q_i$) either choice would be acceptable, the generating function in one case differing from that in the other by an additive term $\Sigma_i w_i\delta_i$. We shall choose a G_2 appropriate to $\bar{n}_i h$ being conjugate to w_i, as in Eq. (4.8) given later.

[9] One first integrates the k integral by parts, before performing the variation. The k (or $p_R/\hbar$) in the integrand depends on E, as in Eq. (A1) of Appendix A, and the computation of $\partial S/\partial E$ in (3.5b) takes cognizance of this fact. The other operations are similar to those described in Appendix A for δG_2 and $\delta\bar{S}$.

[10] H. Goldstein, *Classical Mechanics* (Addison-Wesley, Reading, Mass., 1957), p. 241.

[11] R. Schiller, Phys. Rev. **125,** 1109 (1962).

[12] We first note that at (w^0R_0) the amplitude A_0 of the semiclassical wavefunction in the wR representation is the same for all w^0's (in the unit interval). When one transforms to $\bar{w}\tau$ coordinates then, before the collision, dR equals $p_R^0 d\tau/\mu$ and $\Pi_i d\bar{w}_i$ equals $|\partial\bar{w}_i/\partial w_j^0|\Pi_i dw_i^0$ and hence $|\partial\bar{w}_i/\partial\bar{w}_j^0|\Pi_i d\bar{w}_i^0$, in virtue of (4.15). Since $|\bar{A}_0|^2\Pi_i d\bar{w}_i$ is proportional to $|A_0|^2\Pi_i dw_i^0$ the result in (5.1), apart from a proportionality constant, follows.

[13] Using (4.14) we note that $\bar{w}_j^0$ equals $\partial\bar{S}/\partial(n_j h)$ minus a constant and hence that $\partial\bar{w}_j^0/\partial\bar{w}_i$ equals $\partial^2\bar{S}/\partial n_j\partial\bar{w}_i h$. Further, from (4.13) $\partial\bar{S}/\partial\tau$ equals E, so that $\partial^2\bar{S}/\partial E\partial\tau$ and $\partial^2\bar{S}/\partial n_i\partial\tau$ are unity and zero, respectively. Thus, $\bar{A}$ in Eq. (5.1) can be rewritten as the $(r+1)\times(r+1)$ determinant

$$\bar{A}=|\partial^2\bar{S}/\partial p_0{}^i\partial\bar{q}_i|^{1/2}h^{-1/2}.$$

[14] This type of determinant has been termed[11] a Van Vleck determinant. J. H. Van Vleck, Proc. Natl. Acad. Sci. U.S. **14,** 178 (1928).

[15] V. A. Fock, Vest. Leningrad Univ. Ser. Fiz. Khim. **16,** 67 (1959). An English translation of this paper is available from the National Translations Center, John Crerar Library, 35 West 33rd St., Chicago, Ill. 60616. See Technical Translations **4,** 53 (1960), No. 60-17464.

[16] For a discussion of time-reversal see Ref. 7, pp. 51–57, 169–171.

[17] See, e.g., A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1963), Vol. 2, p. 867.

[18] For purposes of illustration in these figures only, we have treated $\bar{n}$, $\bar{m}$, and k as varying monotonically. They need not do so, as already noted earlier in the text.

[19] $\psi_{nE'}{}^{(+)}(\bar{w}\tau)=\Sigma_m S_{mn}\delta(E-E')\psi_{mE'}{}^{(-)}(\bar{w}\tau)$.

[20] For example, when w is a class II variable, consider the mirror image of the m trajectory of Fig. 2, with the horizontal axis as mirror (that is, change w to $-w$). Beginning at m and at a negative w^0 one can integrate to the turning point and hence to $\bar{m}^T$, and then reflect the curve about the horizontal axis, thus obtaining the curve in Fig. 2(a). In this way a whole series of m trajectories can be obtained, with differing w^T's in the unit interval, and they can then be matched to the same w^T's for the n trajectories.

[21] The following features of rearrangement collisions may be noted. In the flux conservation argument in Part I to determine amplitude A, the w^0 referred to w variables appropriate to reactants and the w referred to w variables appropriate to products; dw^0 was related to dw by trajectories originating in the one and ending in the other. In the FVR the transformation from w to $\bar{w}$ occurs in the products' region, e.g.,[12] and the pre-exponential factor in (7.7) remains well defined. The phase of rearrangement collisions is better calculated using conventional coordinates and then, in the FVR, making a transformation to $\bar{w}$ variables. A detailed discussion of these collisions will be given later.

[22] W. H. Wong and R. A. Marcus, J. Chem. Phys. **55,** 5663 (1971).

[23] The action J_i equals $(n_i+\delta_i)h$, where δ is usually 0 or $\frac{1}{2}$, depending on the degree of freedom.

[24] D. Ter Haar, *Elements of Hamiltonian Mechanics* (North-Holland, Amsterdam, 1961), p. 129, $2\pi\beta_3$ in Fig. 26.

[25] An alternative convention would be to interchange the sin and cos in (9.7), but one would then not get the simple result (9.7), and one would then have to multiply (9.5b) by a phase factor in order to retain a time-reversal significance to the prime notation.

[26] In fact, when $V=0$, the k integrals just cancel the $\frac{1}{2}(n_1+m_1+1)\pi$ term in (7.3), and so behave like this π term with respect to the operations in (9.2).